

DTIC FILE COPY

2

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-01881a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

AD-A229 483

DTIC ECTE

21 1990

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for Public Release
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Department of Chemistry
University of North Carolina6b. OFFICE SYMBOL
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)

Campus Box 3290
Chapel Hill, NC 27599-3290

7b. ADDRESS (City, State, and ZIP Code)

Department of the Navy
Arlington, VA 222178a. NAME OF FUNDING/SPONSORING
ORGANIZATION
Office of Naval Research8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

N0014-89-J-1734

8c. ADDRESS (City, State, and ZIP Code)
800 North Quincy Street
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.PROJECT
NO.TASK
NO.WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification) UNCLASSIFIED:

A Planar Oxocuprate(II) Array Via Heterometallic Alkoxide Chemistry

12. PERSONAL AUTHOR(S) J. A. Samuels, B. A. Vaartstra, J. C. Huffman, K. L. Trojan,
W. E. Hatfield, K. G. Caulton13a. TYPE OF REPORT
Technical Report13b. TIME COVERED
FROM TO14. DATE OF REPORT (Year, Month, Day)
1990 November 1415. PAGE COUNT
1116. SUPPLEMENTARY NOTATION
Technical Report No. 40

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

magnetic susceptibility X-ray diffraction
antiferromagnetic copper oxide
13C NMR zirconium

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Controlled hydrolysis of $K_4Zr_2O(O^iPr)_6$ in the presence of $CuCl_2$ in THF yields $Cu_4Zr_2O_3(O^iPr)_8$, which was characterized by 1H and ^{13}C NMR and infrared spectroscopy, magnetic susceptibility and X-ray diffraction. Cell constants ($-92^\circ C$): $a = 12.673(8) \text{ \AA}$, $b = 17.482(13)$, $c = 10.877(8)$, $\alpha = 104.85(3)$, $\beta = 113.52(3)$, $\gamma = 75.65(3)$ with $Z = 1$ in space group $P1$. The compound has a central planar $Cu_4O_3(O^iPr)_2$ unit terminated on two ends by $Zr_2(O^iPr)_6$ units. The central of the three oxide ions has an unusual planar four-coordinate geometry. The central Cu_4^{8+} unit shows antiferromagnetic coupling, with $\mu_{eff} = 1 \text{ BM/Cu}$ over the range 100-300K. The molecule retains its structure in toluene solution, as judged by 1H and ^{13}C NMR.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

OFFICE OF NAVAL RESERACH

Contract N0014-89-J-1734

R&T Code 4135007---05

TECHNICAL REPORT NO. 40

**A Planar Oxocuprate(II) Array Via Heterometallic
Alkoxide Chemistry**

by

John A. Samuels, Brian A. Vaartstra, John C. Huffman,
Kathleen L. Trojan, William E. Hatfield and Kenneth G. Caulton

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

The Department of Chemistry, The University of North
Carolina at Chapel Hill, North Carolina, 27599, U.S.A.

Prepared for Publication in

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale, its distribution is unlimited.

*This statement should also appear in Item 3 of Document Control
Data - DD Form 1473. Copies of the form are available from the
cognizant contract administrator.

A PLANAR OXOCUPRATE(II) ARRAY VIA
HETEROMETALLIC ALKOXIDE CHEMISTRY

by

John A. Samuels, Brian A. Vaartstra, John C. Huffman,
Kathleen L. Trojan[†], William E. Hatfield and Kenneth G. Caulton^{*}

Department of Chemistry and Molecular Structure Center

Indiana University, Bloomington, IN 47405,

Department of Chemistry, University of North Carolina

Venable and Kenan Laboratories, Chapel Hill, NC 27599

ABSTRACT

Controlled hydrolysis of $K_4Zr_2O(O^iPr)_{10}$ in the presence of $CuCl_2$ in THF yields $Cu_4Zr_4O_3(O^iPr)_{18}$, which was characterized by 1H and ^{13}C NMR and infrared spectroscopy, magnetic susceptibility and X-ray diffraction. Cell constants ($-92^\circ C$): $a = 12.673(8)\text{\AA}$, $b = 17.482(13)$, $c = 10.877(8)$, $\alpha = 104.85(3)$, $\beta = 113.52(3)$, $\gamma = 75.65(3)$ with $Z = 1$ in space group $P\bar{1}$. The compound has a central planar $Cu_4O_3(O^iPr)_2$ unit terminated on two ends by $Zr_2(O^iPr)_8$ units. The central of the three oxide ions has an unusual planar four-coordinate geometry. The central Cu_4^{8+} unit shows antiferromagnetic coupling, with $\mu_{eff} = 1$ BM/Cu over the range 100-300K. The molecule retains its structure in toluene solution, as judged by 1H and ^{13}C NMR.

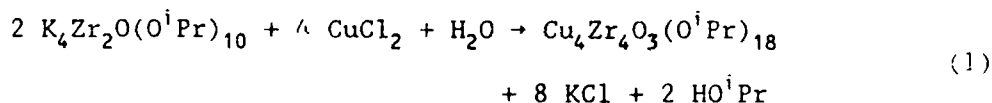
[†] Department of Education Fellow



or	
<input checked="checked" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Application of the molecular precursor method^{1,2} to the synthesis of copper-based high temperature superconductors³ rests on our ability to produce copper-containing heterometallic alkoxides.⁴ We have reported recently^{5,6} on the chemistry of the anion $\text{Zr}_2(\text{O}^i\text{Pr})_9^-$, which is related to recent reports by the group of Mehrotra.^{7,8} We report here our investigation of the coupling of this and related anions to CuCl_2 of relevance to hydrolytic routes to copper/oxo superconductors.

The reaction of $\text{K}_4\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_{10}$,⁶ CuCl_2 , and water (2:4:1 mole ratio) in a refluxing THF solution produces a deep olive green solution. Workup (i.e., removal of solvent, extraction with pentane, concentration, and layering with isopropanol) yields a blue-green solid (25% yield) which was established⁹ to have the formula $\text{Cu}_4^{\text{II}}\text{Zr}_4^{\text{IV}}\text{O}_3(\text{O}^i\text{Pr})_{18}$, **1**, eq. 1. The



centrosymmetric structure is shown in Fig. 1. The molecule contains a planar central $\text{Cu}_4\text{O}_3(\text{O}^i\text{Pr})_2$ unit capped on two opposite ends by $\text{Zr}_2(\text{O}^i\text{Pr})_8$ units. At the crystallographic center of symmetry is an unusual four-coordinate *planar* O^{2-} ion. Only two other examples of this geometry are known.^{10,11} An alternative description of the structure is that two face-shared bi-octahedral $\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_8^{2-}$ units bind through a pseudo-tetrahedral $\mu\text{-O}$ and two terminal O^iPr groups to a central planar $\text{Cu}_4\text{O}(\text{O}^i\text{Pr})_2^{4+}$ unit. This view leads to the idea that the $\text{Zr}_2(\text{O}^i\text{Pr})_8\text{O}^{2-}$ unit is a template (via 2 O^iPr and the oxide) for growth of the planar ribbon of composition $\text{Cu}_4\text{O}(\text{O}^i\text{Pr})_2^{4+}$. Growth of this ribbon into a sheet

(i.e., growth perpendicular to the $(\mu_4-O)_3$ direction) is prevented by the iso-propyl groups on the oxygens which bridge the coppers.

Spectroscopic analysis confirms the chemical formula and structure. IR spectra lack any O-H stretches, thus excluding the presence of hydroxyl or coordinated alcohol. The NMR spectra¹² of 1 lack the expected shifting and broadening associated with paramagnetic species. The methine region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows that the solid-state structure is maintained in solution: the expected five chemical shifts with approximately the correct integral ratio of 2:2:2:2:1 are found.¹² This conclusion is further supported by the methyl-group ^1H and ^{13}C NMR. These are sufficiently complex to indicate the retention of the solid-state structure (with diastereotopic methyls) in solution.

Based on the lack of paramagnetic characteristics in the NMR spectra, the magnetic susceptibility was investigated. This reveals that, while there are unpaired electron spins, these spins are coupled antiferromagnetically. The solution magnetic susceptibility (Evans method, 295K, THF) yields a μ_{eff} of 0.9 BM/Cu. A variable temperature (56-230K) solid-state study shows the μ_{eff} to remain nearly constant at 1.1 BM/Cu from 230-100K, then drop to 0.4 BM/Cu by 56K. A mononuclear Cu^{2+} ion would have $\mu_{\text{eff}} = 1.73$ BM. Our initial exploration of the parameter space of the three J values (two J_{cis} and one J_{trans}) of a Heisenberg Hamiltonian model appropriate to a centrosymmetric Cu_4^{8+} unit shows a singlet ground state. There is another singlet, a set of three triplets, and a quintet state at higher energies; one or more of the triplets become appreciably populated by 100K, causing the rise in μ_{eff} from 56-100K, but up to now it has not been possible to simulate the

magnetic susceptibility data, and further work is in progress. The μ_{eff} fails to rise further even at 300K because a quintet state lies too high to be significantly populated.

This heterometallic oxo alkoxide contains a planar Cu_4 array previously unknown in the chemistry of Cu(II). This work suggests that electropositive partner metals in heterometallic species can "guide" the growth of Cu/O patches which mimic some of the structural features of high T_c superconductors.¹³ We believe that the thermodynamically-favored unit (i.e., Zr_2X_9) of a "partner metal" in a heterometallic alkoxide can serve as a structural template for the planar Cu_4O array. In the present case, three colinear donor sites (i.e., one terminal alkoxide on each Zr together with the $\mu\text{-O}^{2-}$) of two $\text{Zr}_2(\text{O}^i\text{Pr})_8\text{O}^{2-}$ units are complementary to the growth of a copper(II) oxide "ribbon" two coppers wide. Further growth along the ribbon direction (i.e., the 05-05' axis) would require insertion of the repeat unit $\text{Cu}_2\text{O}(\text{O}^i\text{Pr})_2$.

Acknowledgments. This work was supported by DOE grant DE-FG02-88ER-13906, and in part by the Office of Naval Research. We thank Scott Horn for skilled technical assistance.

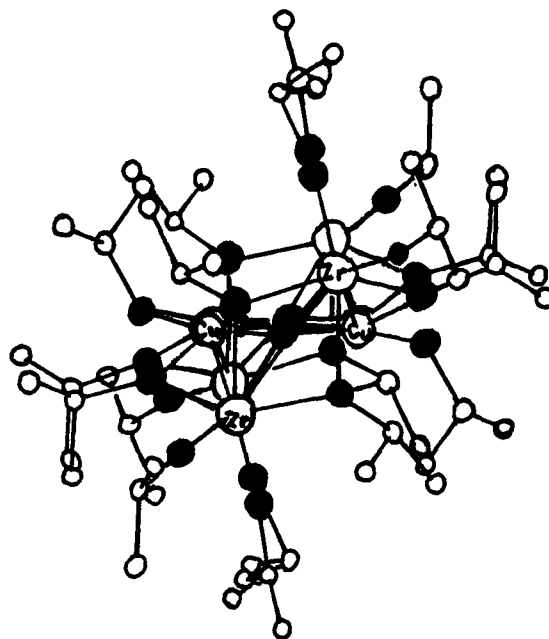
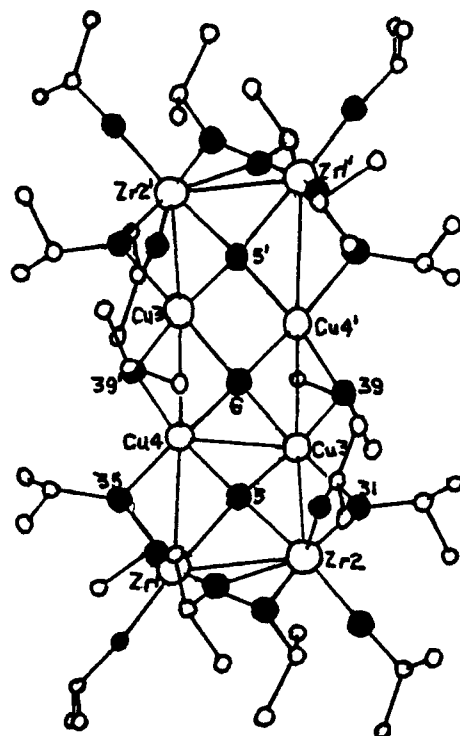
Supplementary Material Available. A table of positional and thermal parameters for compound 1. Ordering information is given on any current masthead page.

REFERENCES

1. Hubert-Pfalzgraf, L. G. *New. J. Chem.* 1987, 11, 663.
2. Bradley, D. C. *Chem. Revs.* 1989, 89, 1317.
3. Bednorz, J. G.; Müller, K. A.; Takashige, M. *Science* 1987, 236, 73.
4. Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Revs.* (in press).
5. Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *J. Chem. Soc., Chem. Comm.* (submitted).
6. Vaartstra, B. A.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* (in press).
7. Dubey, R. K.; Anirudh, S.; Mehrotra, R. C. *J. Organomet. Chem.* 1988, 341, 569.
8. Dubey, R. K.; Singh, A.; Mehrotra, R. C. *Polyhedron* 1987, 6, 427.
9. Crystal data (-92 °C) for $\text{Zr}_4\text{Cu}_4\text{C}_{54}\text{H}_{63}\text{O}_{21} \cdot \text{pentane}$: $a = 12.673(8)\text{\AA}$, $b = 17.482(13)$, $c = 10.877(8)$, $\alpha = 104.85(3)^\circ$, $\beta = 113.52(3)$, $\gamma = 75.65(3)$ with $Z = 1$ in space group $P\bar{1}$. $R(F) = 0.0798$, $R_w(F) = 0.0777$ for 3101 reflections with $F > 2.33\sigma(F)$.
10. Rambo, J. A.; Huffman, J. C.; Christou, G.; Eisenstein, O. *J. Am. Chem. Soc.* 1989, 111, 8027.
11. Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* 1990, 112, 1584.
12. ^1H NMR (500 MHz, 20°, C_6D_6): Methine peaks at 5.51 (septet, $J = 6$ Hz), 5.03 (br), 4.34 (septet, $J = 6$ Hz), 4.21 (m). Methyl peaks at δ 2.53, 2.09, 1.47, 1.26 (all overlapping doublets) and 1.32 (d, $J = 6$). $^{13}\text{C}(^1\text{H})$ NMR (125 MHz, 20°, C_6D_6): δ 72.0, 71.3, 70.0, 66.3, 66.2 (CH, int = 2:2:2:2:1), 33.2 (br), 29.0, 28.4, 27.3 (m), 26.7 (CH_3 , int = 1:1:1:5:1).
13. Cava, R. J. *Science* 1990, 247, 656.

FIGURE CAPTIONS

Figure 1. ORTEP drawing of the nonhydrogen atoms of $\text{Cu}_4\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$. a) viewed perpendicular to the Cu_4O_3 plane and b) viewed along the edge of the Cu_4O_3 plane. Oxygen atoms are stippled. Lines between metals are for clarity, and are not bonds. Primes indicate atoms related by a center of symmetry. Selected structural parameters: Cu3-O6, 1.968(3)Å; Cu4-O6, 1.966(2); Cu3-O5, 1.880(18); Cu4-O5, 1.896(11); Cu3-O39, 1.892(12); Cu4-O39', 1.901(12); Cu3-O31, 1.965(11); Cu4-O35, 1.966(11); Cu3-Cu4 = Cu3-Cu4, 2.781(8); *cis* angles O-Cu-O range from 84.5(5)° to 104.0(5)°.



TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high</u> <u>quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		

ORGANOELEMENT CHEMISTRY - Distribution List

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214
R&T Code 4135002

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907
R&T Code 4135011

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
R&T Code 4135014

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
R&T Code 4135007

Professor M. Frederick Hawthorne
Department of Chemistry
405 Hilgard Avenue
University of California
Los Angeles, CA 90024
R&T Code 4135004

Professor Robert H. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, TX 76843
R&T Code 4135005

Professor Kurt Niedenzu
Department of Chemistry
University of Kentucky
Lexington, KY 40506
R&T Code 4135003

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706
R&T Code 4135008